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(54) **Perfume microcapsules for use in granular detergent compositions.**

(57) Perfume-containing microcapsules coated with a water-insoluble cationic fabric softener and used in granular detergent compositions effectively impart perfume to fabrics during the home laundering operation. A method for delivery of the perfume is also provided.

**EP 0 376 385 A2**

## PERFUME MICROCAPSULES FOR USE IN GRANULAR DETERGENT COMPOSITIONS

TECHNICAL FIELD

5 The present invention relates to certain coated perfume-containing microcapsules which when used in granular laundry detergent compositions effectively deliver perfume to fabrics during the home laundering operation. The microcapsules containing the perfume are coated with a water-insoluble cationic fabric softener to facilitate attachment of the capsules to fabrics during a presoak bath or in the washing machine. The capsules thereafter release the perfume by diffusion through the capsule wall and by rupturing of the capsules during manipulation of the fabrics.

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BACKGROUND OF THE INVENTION

15 Delivery of perfumes, particularly volatile and nonsubstantive perfumes, to fabrics during the laundering operation is difficult. Surfactants are generally employed during presoaking and washing steps for the purpose of removing materials (soil) from the fabrics. Simultaneous deposition onto fabrics of perfume can, therefore, prove troublesome. Moreover, retention of perfumes, particularly the volatile and nonsubstantive perfumes, on fabrics during the drying process remains difficult.

20 Although treatment of fabrics with microcapsules is known (see, for example, Ida et al, U.S. Patent 3,870,542, issued March 11, 1975; and Pandell et al, U.S. Patent 3,632,296, issued January 4, 1972), such prior art fabric treatment has generally required utilization of large numbers of microcapsules to provide effective capsule delivery.

25 U.S. Patent 4,234,627, Schilling, issued November 18, 1980, and U.S. Patent 4,145,184, Brain et al, issued March 20, 1979, disclose granular compositions containing friable microcapsules containing conditioning agents, including perfumes, to deliver such conditioning agents to fabrics during the presoaking/washing stage of the home laundry operation.

Despite these disclosures, there is a continuing need for improved compositions capable of more effectively delivering perfumes to fabrics.

30 Accordingly, it is an object of the present invention to provide improved perfume-containing microcapsules which when used in granular presoaking/washing detergent compositions deliver effective amounts of perfume to fabrics being laundered.

It is a further object of the present invention to provide an improved method for delivering perfume to fabrics during the presoak or wash stage of the laundering process.

35 It has been surprisingly discovered that by utilizing particular types of perfume-containing microcapsules coated with water-insoluble cationic fabric softeners, the above objectives can be attained.

SUMMARY OF THE INVENTION

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The present invention relates to microcapsules having an average size of from about 5 to 500 microns, each microcapsule consisting essentially of:

- (i) a liquid core containing perfume; and
- 45 (ii) a solid thin polymeric shell completely surrounding said core, said shell having an average thickness of from about 0.1 to 50 microns, and said shell being formed by complex coacervation of polycationic and polyanionic materials; said microcapsules being coated with a substantially water-insoluble cationic fabric softener having a melting point between about 40°C and 150°C, wherein the weight ratio of microcapsules to cationic softener is from about 3:1 to about 50:1.

50 The invention also relates to granular laundry detergent compositions comprising from about 0.1% to 20% of the above coated perfume-containing microcapsules and from about 5% to 99% by weight of a detergent adjuvant selected from the group consisting of water-soluble deterative surfactants, detergency builders, and mixtures thereof.

Additionally, the present invention relates to a method of treating fabrics with compositions as described above.

DETAILED DESCRIPTION OF THE INVENTION

5 The present invention involves the home laundry application to fabrics of granular detergent compositions containing perfume microcapsules coated with a water-insoluble cationic softener. The cationic fabric softener facilitates attachment of the capsules to fabrics during a presoak bath or in the washing machine. The capsules thereafter release the perfume by diffusion through the capsule wall and by manipulation of the treated fabrics so as to rupture the capsules. While not intending to be limited by theory, it is believed that the cationic softener complexes with the anionic polymer portion of the capsule wall so as to enhance 10 diffusibility of the perfume during the fabric laundering process when the capsules are rehydrated by the laundering solution. This results in improved delivery of the perfume to fabrics during the washing and/or drying steps, as desired.

Microcapsules

15 The microcapsules useful in the present invention comprise a liquid core containing one or more perfumes and a thin polymeric shell, formed by complex coacervation of polycationic and polyanionic materials, completely surrounding the liquid core. By encapsulating the perfume (in liquid form), the perfume is protected during the production, distribution and storage of the granular detergent composition and is thus preserved for most efficient application to fabrics during the laundering operation. Perfume is actually applied to the fabrics by diffusion through the capsule wall or when the microcapsules rupture during manipulation of the fabrics. This can occur either during the automatic washing or drying step of the 25 home laundering operation or can actually occur after the fabrics are laundered and while they are being used.

The perfume which can be used in the liquid cores of the microcapsules can be any water-insoluble (or substantially water-insoluble) odoriferous material and will be selected according to the desires of the formulator. (Water-soluble perfume components are difficult to encapsulate using the complex coacervation 30 methods described hereinafter.) In general terms, such perfume materials are characterized by a vapor pressure above atmospheric pressure at ambient temperatures. The perfume materials employed herein will most often be liquid at ambient temperatures, but also can be solids such as the various camphoraceous perfumes known in the art. A wide variety of chemicals are known for perfumery uses, including materials such as aldehydes, ketones, esters, and the like. More commonly, naturally-occurring plant and animal oils 35 and exudates comprising complex mixtures of various chemical components are known for use as perfumes, and such materials can be used herein. The perfumes herein can be relatively simple in their composition, or can comprise highly sophisticated, complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odor.

Typical perfumes herein can comprise, for example, woody/earthy bases containing exotic materials 40 such as sandalwood oil, civet, patchouli oil, and the like. The perfumes herein can be of a light, floral fragrance, etc., rose extract, violet extract, and the like. The perfumes herein can be formulated to provide desirable fruity odors, e.g., lime, lemon, orange, and the like. In short, any material which exudes a pleasant or otherwise desirable odor can be used in the liquid microcapsule core to provide a desirable odor when applied to fabrics. Preferred, perfumes include musk ambrette, musk ketone, musk tibetine, musk xylol, 45 aurantol, ethyl vanillin and mixtures thereof. Examples of such perfume materials can be found in U.S. Patent 4,515,705, Moeddel, issued May 7, 1985, incorporated herein by reference.

Perfumes will frequently be in liquid form and can be used as the sole materials in the microcapsule core. Perfumes which are normally solid can also be employed in the microcapsule core if they are admixed with a liquefying agent such as a solvent. Any organic solvent can be used to liquify normally solid 50 perfume for use in the microcapsule core provided such a solvent is chemically compatible with the microcapsule shell material described hereinafter. Preferred solvents for use herein are materials such as mineral oil and dodecane.

The shell material surrounding the liquid, perfume-containing core to form the microcapsule can be any suitable polymeric material formed by complex coacervation of polycationic and polyanionic materials. The 55 shell is substantially impervious to the materials in the liquid core and to materials which may come in contact with the outer surface of the shell during storage. When the microcapsules are rehydrated by the laundering solution, it is believed that pores in the microcapsules expand to allow diffusion of the perfume during the washing and drying steps, thereby improving perfume delivery to fabrics.

Suitable polycationic materials for use in forming the polymeric shell of the microcapsules herein include materials such as gelatin, poly(vinyl pyrrolidone), poly(ethyleneimine) and albumin. Type A gelatin is preferred. Suitable polyanionic materials for forming the polymeric shell include materials such as gum arabic, poly(ethylene/maleic anhydride), poly(vinyl methylethyl maleic anhydride), polyphosphate, polyacrylate, and gelatin. Polyphosphates, especially sodium hexametaphosphate, are particularly preferred.

Microcapsules as described above can be prepared by any conventional complex coacervation process. Such methods are described in U.S. Patent 2,800,457; 3,190,837; 3,317,434; 3,341,466; 3,533,958; 3,687,865; 3,697,437; and 3,840,467. All of the above patents are incorporated herein by reference.

The microcapsules should have an average size of between about 5 microns and 500 microns, preferably between about 40 microns and 250 microns, more preferably between about 80 and 150 microns. Furthermore, the capsules utilized in the present invention have an average shell thickness ranging from about 0.1 to 50 microns, preferably from about 0.4 to 30 microns.

The microcapsules of the present invention are generally friable in nature. Friability refers to the propensity of the microcapsules to rupture or break open when subjected to direct external pressures or shear forces. For purposes of the present invention, the microcapsules utilized are "friable" if, while attached to fabrics treated therewith, they can be ruptured by the forces encountered when the capsule-containing fabrics are tumbled in an automatic laundry dryer or are manipulated by being worn or handled. Microcapsules made with the above-described shell materials will be "friable" if they fall within the capsule size and shell thickness limitations provided above.

#### Cationic Fabric Softener

Attachment of the above-described microcapsules to the fabrics being treated therewith is facilitated by surrounding the microcapsules with the cationic fabric softener. These are substantially water-insoluble materials which are fabric substantive and which have a melting point with the range of from about 40° C to 150° C, preferably with the range of from about 49° C to 105° C. By "substantially water-insoluble" herein is meant a water insolubility of 1% by weight, or less, at 30° C.

Suitable cationic capsule transfer agents include any of the cationic (including imidazolinium) compounds listed in U.S. Patent No. 3,686,025, Morton, issued August 22, 1972, incorporated herein by reference. Such materials are well known in the art and include, for example, the quaternary ammonium salts having at least one, preferably two, C<sub>10</sub>-C<sub>20</sub> fatty alkyl substituent groups; alkyl imidazolinium salts wherein at least one alkyl group contains a C<sub>8</sub>-C<sub>25</sub> carbon "chain"; the C<sub>12</sub>-C<sub>20</sub> alkyl pyridinium salts, and the like.

Preferred cationic softeners herein include the quaternary ammonium salts of the general formula R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>R<sup>4</sup>N<sup>+</sup>X<sup>-</sup>, wherein groups R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are, for example, alkyl, and X<sup>-</sup> is an anion, e.g., halide, methylsulfate, and the like, with the chloride and methylsulfate salts being preferred. Especially preferred capsule transfer agents are those wherein R<sup>1</sup> and R<sup>2</sup> are each C<sub>12</sub>-C<sub>20</sub> fatty alkyl and R<sup>3</sup> and R<sup>4</sup> are each C<sub>1</sub>-C<sub>4</sub> alkyl. The fatty alkyl groups can be mixed, i.e., the mixed C<sub>14</sub>-C<sub>18</sub> coconutalkyl and mixed C<sub>15</sub>-C<sub>18</sub> tallowalkyl quaternary compounds. Alkyl groups R<sup>3</sup> and R<sup>4</sup> are preferably methyl.

Exemplary quaternary ammonium softeners herein include ditallowalkyldimethylammonium methylsulfate, ditallowalkyldimethylammonium chloride, dicoconutalkyldimethylammonium methylsulfate, and dicoconutalkyldimethylammonium chloride.

The above-described microcapsules are coated with the fabric softener such that the weight ratio of microcapsules to softener generally varies between about 50:1 to 3:1, preferably between about 20:1 and 4:1, more preferably between about 10:1 and 5:1.

It is preferred that the fabric softener completely surround or envelop the individual microcapsules. This is generally accomplished by thoroughly admixing the microcapsules with the softener in some form of liquid medium, and then drying to solidify the coating. Any conventional coating technique can also be utilized including spray-on processes or fluidized bed coating methods, which are preferred for commercial scale operation.

The cationic fabric softener coating can optionally include minor amounts (e.g., less than 50%, preferably less than 20%) by weight of the nonionic capsule transfer agents described in U.S. Patent 4,234,627 to Schilling, incorporated herein by reference.

#### Granular Detergent Composition

Granular laundry detergent presoaking and/or washing compositions herein contain from about 0.1% to 20%, preferably from about 0.3% to about 10%, more preferably from about 0.5% to about 5%, by weight of the above coated perfume-containing microcapsules. Such compositions also contain from about 5% to about 99%, preferably from about 10% to about 90%, more preferably from about 20% to about 80%, by weight of a detergent adjuvant selected from the group consisting of water-soluble deterative surfactants, detergent builders, and mixtures thereof.

Water-soluble surfactants used in the presoaking/washing detergent compositions herein include any of the common anionic, nonionic, ampholytic and zwitterionic deterative surfactants well known in the detergent arts. Mixtures of surfactants can also be employed herein. More particularly, the surfactants listed in Booth, U.S. Patent No. 3,717,630, issued February 20, 1973, and Kessler et al; U.S. Patent No. 3,332,880, issued July 25, 1967, each incorporated herein by reference, can be used herein. Non-limiting examples of surfactants suitable for use in the instant compositions are as follows.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols ( $C_8$ - $C_{18}$  carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patent Nos. 2,220,099, and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as  $C_{11-13}$  LAS.

Other anionic surfactants herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Water-soluble nonionic surfactants are also useful in the compositions of the invention. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to 12 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionic surfactants are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration.

with from 3 to 12 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 4 to 8 moles of ethylene oxide per mole of alcohol.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic, quaternary, ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

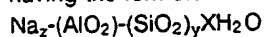
When the present granular detergent compositions are used as presoaking or wash additive compositions in conjunction with other commercially available laundry detergent products, the deterative surfactant component generally comprises from about 0% to 20% by weight of the compositions, preferably from about 1% to 10% by weight. When the present compositions are to be used as the sole detergent product during the laundering process, the deterative surfactant component generally comprises from about 5% to about 75%, preferably from about 10% to 40%, by weight of the composition.

In addition to detergent surfactants, detergency builders can be employed in the final granular detergent product. Water-soluble inorganic or organic electrolytes are suitable builders. The builder can also be water-insoluble calcium ion exchange materials; nonlimiting examples of suitable water-soluble, inorganic detergent builders include: alkali metal carbonates, borates, phosphates, bicarbonates and silicates. Specific examples of such salts include sodium and potassium tetraborates, bicarbonates, carbonates, orthophosphates, pyrophosphates, tripolyphosphates and metaphosphates.

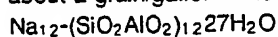
Examples of suitable organic alkaline detergency builders include: (1) water-soluble amino carboxylates and aminopolyacetates, for example, nitrilotriacetates, glycinate, ethylenediamine, tetraacetates, N-(2-hydroxyethyl)nitrilo diacetates and diethylenetriamine pentaacetates; (2) water-soluble salts of phytic acid, for example, sodium and potassium phytates; (3) water-soluble polyphosphonates, including sodium, potassium, and lithium salts of ethane-1-hydroxy-1, 1-diphosphonic acid; sodium, potassium, and lithium salts of ethylene diphosphonic acid; and the like; (4) water-soluble polycarboxylates such as the salts of lactic acid, succinic acid, malonic acid, maleic acid, citric acid, carboxymethyloxysuccinic acid, 2-oxa-1,1,3-propane tricarboxylic acid, 1,1,2,2-ethane tetracarboxylic acid, mellitic acid and pyromellitic acid; and (5) water-soluble polyacetals as disclosed in U.S. Patent Nos. 4,144,266 and 4,246,495 incorporated herein by reference.

Another type of detergency builder material useful in the final granular detergent product comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations preferably in combination with a crystallization seed which is capable of providing growth sites for said reaction product. Such "seeded builder" compositions are fully disclosed in British Patent No. 1,424,406.

A further class of detergency builder materials useful in the present invention are insoluble sodium aluminosilicates, particularly those described in Belgian Patent No. 814,874, issued November 12, 1974, as having the formula:



wherein z and y are integers equal to at least 6, the molar ratio of z to y is in the range of from 1.0:1 to about 0.5:1, and X is an integer from about 15 to about 264, said aluminosilicates having a calcium ion exchange capacity of at least 200 milligrams equivalent/gram and a calcium ion exchange rate of at least about 2 grain/gallon/minute/gram. A preferred material is Zeolite A which is:



When the present granular detergent compositions are used as presoaking or wash additive compositions in conjunction with other commercially available laundry detergent products, the detergency builder component generally comprises from about 20% to 90% by weight of the compositions, preferably from about 30% to 75% by weight. When the present granular compositions are to be used as the sole detergent product during the laundering process, the detergency builder component generally comprises from about 10% to about 75%, preferably from about 20% to 50%, by weight of the composition.

Optional detergent composition components include enzymes (e.g., proteases and amylases), bleaches

and bleach activators, soil release agents (e.g., methylcellulose), soil suspending agents (e.g., sodium carboxymethylcellulose), fabric brighteners, enzyme stabilizing agents, color speckles, suds boosters or suds suppressors, anticorrosion agents, dyes, fillers, germicides, pH adjusting agents, nonbuilder alkalinity sources, and the like.

## EXAMPLE 1

A granular laundry detergent composition of the present invention is as follows.

Ingredient	Weight Percent
Sodium C <sub>13</sub> linear alkylbenzene sulfonate	8.5
Sodium C <sub>14-15</sub> alkyl sulfate	8.4
Sodium tripolyphosphate	39.4
Sodium carbonate	12.3
Sodium silicate (1.6 ratio)	5.6
Water	7.0
Coated perfume microcapsules	0.9
Sodium sulfate & miscellaneous	Balance to 100

The above granular detergent composition is made by mixing the ingredients (except the microcapsules) in a crutcher, and then spray-drying by conventional methods.

The coated perfume microcapsules are made as follows: A 67/33 (by weight) perfume/light mineral oil (viscosity 125/135) mixture is heated to about 60 °C in a constant temperature controlled water bath. About 10 grams of Type A gelatin per 100 grams of perfume/mineral oil is dissolved in 250 ml of distilled water with stirring at 250 revolutions per minute (rpm). About 0.5 to 1.0 grams of sodium hexametaphosphate per 100 grams of perfume/mineral oil is dissolved in distilled water to a concentration of 5% by weight. The dissolved gelatin solution is stirred at 600 rpm using a Lightin Stirrer Model RP1515 with a 5 cm high sheer stirring blade. The perfume/mineral oil mixture is added dropwise to the gelatin solution over a period of 10-15 minutes to form an emulsion with particle sized ranging from 75-250 microns. An additional 200 ml of 60 °C water is added and the stirring speed reduced to 250 rpm. The pH of the mixture is adjusted to 4.92 with glacial acetic acid. The heating element of the water bath is turned off to allow the mixture to cool for from 6 to 24 hours. When the oil droplets are completely covered with a layer of gelatin the reaction is cooled to 1-2 °C with external ice. The mixture is allowed to remain at that temperature for 10 to 30 minutes. At this point 4 ml of 25% glutaraldehyde is added to crosslink the gelatin capsule walls. The mixture is then stirred and allowed to warm to room temperature for from 6 to 24 hours. Approximately 4 grams of a syloid filter aid is added to the mixture after the reaction with glutaraldehyde is completed. The mixture is then filtered to separate the capsules. The capsules are washed with 2 liters of water to remove residual glutaraldehyde. The capsules are then spread on a paper towel to dry. (Drying can also be accomplished in a fluid bed dryer when larger than 100 gram samples are used.) The capsules are then sieved to remove capsules and debris of a size larger than about 250 microns. The remaining capsules have an average size of about 100 to 150 microns and have a shell thickness averaging 0.1 to 50 microns.

The capsules are added to a solution of methylene dichloride containing ditallowdimethylammonium chloride (DTDMAC) in a ratio of 10 ml of methylene dichloride and 2 grams of DTDMAC per 10 grams of capsules. The methylene chloride is removed from the mixture using a stream of nitrogen. The coating solution is warmed gently in a steam bath to facilitate removal of the solvent. The resulting capsules are evenly coated with a thin layer (about 20-50 microns) of the DTDMAC. (For larger samples, a Wurster Coater or any suitable fluid bed apparatus can be used to obtain an even coating of the microcapsules, after adjustment of all ratios to obtain an even flow of the capsules in the system.)

The microcapsules are then admixed with the spray dried detergent ingredients to form a finished detergent composition.

When the composition is used in a washing machine to clean fabrics, the coated perfume-containing microcapsules effectively deliver perfume to the fabrics during the washing and drying steps and thereafter during handling of the fabrics.

Other compositions of the present invention are obtained when the perfume microcapsules are prepared

by initially using a 50/50 (by weight) perfume/light mineral oil mixture, or 100% perfume (no mineral oil), or by replacing the sodium hexametaphosphate with gum arabic.

Other compositions herein are obtained when the DTDMAC used to coat the microcapsules is replaced with a 3:1 by weight ratio mixture of DTDMAC and tallow alcohol, or when the sodium tripolyphosphate in the detergent composition is replaced with a 3:1 by weight ratio mixture of hydrated sodium zeolite A and sodium carbonate.

## EXAMPLE II

A granular laundry detergent composition of the present invention is as follows..

Ingredient	Weight Percent
1. Spray-dried detergent base granules:	
Sodium C <sub>13</sub> linear alkylbenzene sulfonate (70%)/Sodium C <sub>14-15</sub> alkyl sulfate (30%)	12.88
Sodium tripolyphosphate	4.56
Tetrasodium pyrophosphate	17.16
Sodium silicate (1.6 ratio)	7.20
Diethylenetriamine pentaacetic acid	0.38
Brightener	0.18
Sodium polyacrylate (MW 4500)	0.96
Polyethylene glycol (MW 8000)	0.29
Water*	3.0
Sodium sulfate & miscellaneous	Balance to 100
2. Spray on base granules:	
C <sub>12-13</sub> alcohol polyethoxylate (6.5)**	0.44
3. Admix with base granules:	
Sodium carbonate	22.00
Enzyme-Savinase (Novo)	0.37
Sodium perborate monohydrate (solids)	3.69
Nonanoyloxybenzene sulfonate	5.26
Coated perfume microcapsules	1.50

\*Remaining water is brought in with admixes.

\*\*Alcohol and monoethoxylated alcohol removed.

The above granular detergent composition is made as follows. The spray-dried detergent base granules are formed by mixing the ingredients of step 1 in a crutcher, and then spray-drying by conventional methods. The nonionic surfactant of step 2 is then sprayed onto the detergent base granules. The resulting product is admixed with the ingredients of step 3, including the coated perfume microcapsules made according to Example I, to form a finished detergent composition.

When the composition is used in a washing machine to clean fabrics, the coated perfume-containing microcapsules effectively deliver perfume to the fabrics during the washing and drying steps and thereafter during handling of the fabrics.

## Claims

1. Microcapsules having an average size of from 5 to 500 microns, characterized in that each microcapsule comprises:

- (i) a liquid core containing perfume; and
- (ii) a solid thin polymeric shell completely surrounding said core, said shell having an average thickness of from 0.1 to 50 microns, and said shell being formed by complex coacervation of polycationic and



polyanionic materials;

said microcapsules being coated with a substantially water-insoluble cationic fabric softener having a melting point between 40° C and 150° C, wherein the weight ratio of microcapsules to cationic softener is from 3:1 to 50:1.

5 2. Microcapsules according to Claim 1 wherein the microcapsule shell wall material is formed by complex coacervation of Type A gelatin and gum arabic or polyphosphate materials.

3. Microcapsules according to Claim 1 wherein the cationic fabric softener is a C<sub>12</sub>-C<sub>20</sub> dialkyldimethylammonium salt.

4. Microcapsules according to Claim 3 wherein the weight ratio of the microcapsules to the cationic fabric softener is from 4:1 to 20:1, preferably 5:1 to 10:1.

10 5. Microcapsules according to any of Claims 1-4 having an average size of from 80 to 150 microns.

6. A granular laundry detergent composition comprising 5% to 99% by weight of a detergent adjuvant selected from the group consisting of water-soluble deterative surfactants, detergency builders, and mixtures thereof, said composition being characterized in that it contains from 0.1% to 20% by weight of perfume microcapsules having an average size of from 5 to 500 microns, each microcapsule consisting essentially of:

15 (i) a liquid core containing perfume; and  
(ii) a solid thin polymeric shell completely surrounding said core, said shell having an average thickness of from 0.1 to 50 microns, and said shell being formed by complex coacervation of polycationic and polyanionic materials;

20 said microcapsules being coated with a substantially waterinsoluble cationic fabric softener having a melting point between 40° C and 150° C, wherein the weight ratio of microcapsules to catonic softener is from 3:1 to 50:1.

7. A composition according to Claim 6 wherein the microcapsule shell wall material is formed by complex coacervation of Type A gelatin and gum arabic or polyphosphate materials, and wherein the cationic fabric softener is a C<sub>12</sub>-C<sub>20</sub> dialkyldimethylammonium salt at a weight ratio of the microcapsules to the cationic fabric softener from 20:1 to 4:1.

8. A composition according to Claim 6 comprising from 20% to 80% by weight of the detergent adjuvant.

30 9. A composition according to Claim 8 comprising from 10% to 40% by weight of the deterative surfactant and from 20% to 50% by weight of the detergent builder.

10. A process for treating fabrics comprising contacting said fabrics with a laundering solution comprising an effective amount of a composition according to Claim 6.

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(54) **Perfume microcapsules for use in granular detergent compositions.**

(57) Perfume-containing microcapsules coated with a water-insoluble cationic fabric softener and used in granular detergent compositions effectively impart perfume to fabrics during the home laundering operation. A method for delivery of the perfume is also provided.

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# EUROPEAN SEARCH REPORT

Application Number

EP 89 20 3260

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
X	FR-A-2 333 042 (THE PROCTER & GAMBLE CO.) * the whole document, particularly page 2, lines 27-39; page 3, lines 1-12; page 4, lines 5-10; page 6, lines 33-40; page 7, lines 1-5 *	1-10	C 11 D 17/00 C 11 D 3/50 C 11 D 3/37 C 11 D 1/62 C 11 D 17/08
A	FR-A-2 584 088 (LION CORPORATION) * claims *	1,2,5,6 8-10	
A	FR-A-2 143 832 (THE PROCTER & GAMBLE CO.) * claims; page 11, lines 34-40; page 12, lines 1,2 *	1,2,5,6 8-10	
A	EP-A-0 038 985 (BAYER AG) * abstract; page 5, lines 1-23; claims *	1,2,5,6 8-10	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			C 11 D
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 09-07-1990	Examiner PELLI-WABLAT B
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... * : member of the same patent family, corresponding	

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